SCIENCE FOR CERAMIC PRODUCTION

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HIGH DENSITY TECHNICAL CERAMICS: TECHNOLOGY AND PREPARATION OF GREEN ARTICLES FOR SINTERING[1]

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It is shown that the degree of aggregation of powders and the properties of aggregates (size, strength, porosity) affect the degree of sintering and the microstructure characteristics of the ceramic fabricated. The conditions for obtaining low-aggregation powder and methods for de-aggregating powder are examined. The requirements which powders must satisfy in order to obtain compacts with a uniform pore size and uniform sintering over the volume of the articles are formulated.

The advances made in obtaining modern technical ceramics are due, first and foremost, to the development of a technology for obtaining highly dispersed powders and the development of a theory of sintering. For such powders, the most likely mechanism of sintering is thought to be sliding and adjustment of the boundaries of highly dispersed particles with the boundaries simultaneously undergoing deformation by means of volume diffusion. This is called “hot self-pressing” because of the large surface tension forces [1], so that the main condition for fabricating high-density materials is high dispersity of the powder [2]. Such a mechanism can operate only for high values of the diffusion coefficient, which determines the possibility of boundary adjustment by a change in the shape of the particles. This is promoted, first and foremost, by a high concentration of vacancies and the presence of high stresses in the lattice during modification [3, 4]. The first condition can be satisfied by introducing heterovalent additives into the oxides and the second by introducing isovalent oxides.

The chemical purity of the initial material (reagents, diluents) strongly influences the quality of the ceramic materials obtained. No less important is the preservation of high purity during the production of the oxide powder and the ceramic from this oxide. Experience shows that to achieve high and reproducible property indicators the total content of the impurities in the ceramic must not exceed 0.01%.

One of the main questions in the technology of high-quality materials is the choice of optimal techniques for obtaining the intermediate product. The structure of the compacts determines the degree and uniformity of pore removal during sintering and the attainment of a prescribed structure for the article. The main properties of the intermediate product formed are the porosity and its volume distribution as well as the maximum size and the size distribution of the pores. These indicators depend on the structure of the initial powders, which must consist of spherical aggregates with the minimum, identical size (< 1 – 2 μm). The methods used to form the articles must give uniform particle packing without substantial stresses and make it possible to obtain compacts with uniform density and pores with approximately the same size. Such a structure prevents differentiated (zonal) sintering and gives a uniformly crystalline microstructure after sintering [5]. These principles are general for oxides and their compounds and are confirmed by many examples of sintering of different materials, and especially clearly for sintering of optically transparent and construction ceramics. Thus, the presence of 5 μm and larger particles in the initial powders, even in small quantities (5 – 10%), engenders nonuniformity of microstructure and optical properties of optical ceramics and a large decrease of mechanical strength in construction ceramics because of enlargement of crystals near large aggregates.

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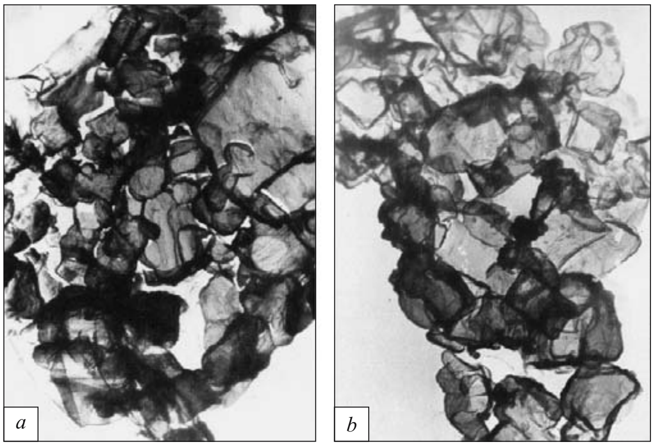

Fig. 1. Aggregates of commercial powders of scandium (*a*) and yttrium (*b*) oxides, × 10,000.

The structure of powder — size, density, and strength of the particles and aggregates — determines the post-sintering quality of the ceramic [2, 6]. For example, commercial powders consist of large, strong, porous aggregates even though the particle dispersity is high (specific surface area up to 10 – 15 m^2/g), and this makes it difficult to sinter compacts to high density. As an example, photographs of commercial powders of scandium and yttrium oxide are displayed in Fig. 1.

In industry and laboratory practice, the initial oxides and their compounds are ordinarily obtained by thermal decomposition of low-solubility compounds, for example, oxalates, hydroxides, and carbonates, which transform into oxides at comparatively low temperatures without corrosive gaseous products being released. Although they are intermediate elements in the technology, their properties have a large effect on the characteristics of the powders obtained from them.

The most important indicators of the intermediate compounds are their chemical and phase compositions as well as the structure of the powders. The main parameters are their dispersity and the degree of aggregation as well as the size, density, and strength of the aggregates. Oxide powders "inherit" them during calcination. Transformations of one solid phase into another are accompanied by various physical – chemical processes: chemical reactions occur, the crystal lattice of the compound is reborn, the density of surface defects, the size and volume of the particles, and the strength of the particles and aggregates all change, and so forth. At the present time powders are obtained primarily by two methods: precipitation in the form of hydroxides, oxalates, or carbonates from salt solutions and the heterophase interaction of a solid soluble salt with a solution containing anions of the compound obtained. The structure and properties of the precipitated powders are determined completely by the precipitation conditions, depending on which large-crystalline or highly dispersed amorphous precipitates can be obtained.

The heterophase method yields powders of low-solubility compounds, which repeat the structure of the initial salts, since formation occurs by the creation of a new phase on the surfaces of the particles of the initial salts with their morphology being repeated. When these compounds are converted into oxides, all structural elements of the powders of low-solubility compounds are inherited. Thus, the degree of sintering, the microstructure, and the properties of a ceramic can be regulated at the initial, preliminary stages.

We believe, on the basis of accumulated experience, that the precipitation method where concentrated salt solutions are injected into a concentrated solution of a precipitant is essentially a universal method for producing powders of different multicomponent oxide systems that gives high particle dispersity (no aggregates larger than 1 μm) and a uniform distribution of the components. After precipitation the powders are characterized by good technological properties: high filtration coefficient, no aggregation during drying, brief subsequent comminution, and so on; the powders do not aggregate in storage. This method is simple to use, does not require special, complicated equipment, and can be used to obtain most highly heat resistant oxides and their compounds. The equipment can be improved by developing a special high-temperature dispersing reactor which traps the corrosive gases that form — nitrogen or sulfur chlorides, oxides. The size of the aggregates in this case is determined by the size of the particles being dispersed. The most promising and ecologically clean process is injection into the reactor a suspension of highly dispersed hydroxides; this yields oxide particles with a prescribed dispersity without corrosive gases being released.

The following stages of the two basic processes for obtaining oxide powders are the stages at which particle aggregation is observed:

production of low-solubility compounds: during chemical precipitation from diluted solutions, especially from hot solutions; during aging of the precipitate in the mother solution; during chemical precipitation from concentrated solutions in the case where there is a substantial temperature difference between the salt and precipitant solutions; during heterophase synthesis from the aggregated initial salt;

heat treatment of low-solubility compounds: during calcination of aggregated low-solubility compounds; during calcination of various aggregated salts; during calcination of low-solubility compounds and salts, as a result of surface diffusion.

de-aggregation methods: wet comminution of oxides, wet comminution aggregated intermediate compounds, comminution of soluble salts in organic liquids prior to their conversion into low-solubility compounds during heterophase interaction and during direct calcination for conversion into oxides.

Injection of concentrated hot solutions of salts into a concentrated solution of a precipitating agent is a promising

TABLE 1.

Indicator	Scandium oxide powder		Yttrium oxide powder	
	No. 1	No. 2	No. 1	No. 2
Powder:				
specific surface area, m^2/g	20.6	40.5	16.0	18.8
size of aggregates, μm	20 – 35	5 – 10	5 – 10	10 – 15
x-ray density, g/cm^3	3.83	3.83	5.03	5.03
pycnometric density, g/cm^3	3.60	3.65	4.75	4.78
refractive index of crystals	1.83	1.87	1.85	1.86
Ceramic,* relative density of the samples, %	77.2**	94.0**	94.4***	87.0***

* The refractive index of the crystals in the ceramic is 1.91 in all cases.

** The samples were pressed under pressure 400 MPa and vacuum sintered at 1700°C.

*** The samples were pressed under pressure 200 MPa and sintered in a flame furnace at 1650°C.

method for obtaining powders that do not require de-aggregation.

The strongest aggregates of oxide particles are formed when intermediate compounds are obtained by precipitation from diluted hot solutions; such powders retain their high strength when they undergo calcination. Strong aggregates are also formed during calcination of different compounds in cases where aggregation occurs as a result of surface diffusion processes.

An effective method for de-aggregating powders is comminution of the intermediate compounds in water or inorganic liquids prior to calcination.

Crystals of commercial oxide powders do not all have the same degree of perfection. This is evidenced by the large differences in their pycnometric density and refractive index, which are always much less than the corresponding x-ray density and refractive index of crystals with perfect structure [7]. Some characteristics of commercial yttrium and scandium oxide powders as well as ceramics are presented in Table 1.

As a result of the presence of strong porous aggregates in commercial powders, local porous sections appear in the compacts; these sections cannot be completely removed during sintering, since a strong framework is formed. In this connection, the mobility of particles, bound with one another, is limited and the porosity of the material is always quite high after sintering. Such aggregates, in addition, are distinguished by substantial strength. This is probably a result of inheriting large-crystalline, aggregated, intermediate products, since precipitation of the latter is conducted, as a rule, from low-concentration solutions during heating.

In some cases, the powders can consist of nonporous aggregates. Then the density of a compact is found to be elevated in these sections. On sintering, particles merge and individual large crystals are formed in a mass of fine crystals; this results in nonuniform and anomalous particle growth. The microstructure of the ceramic is distinguished by substantial nonuniformity. This is comprises the inherited succession of the structure of the preceding solid phase, which determines the structure of the subsequent (intermediate) and then final product to which its properties are transmitted.

As an example, we present the microstructural characteristics of a ceramic consisting of yttrium – aluminum garnet sintered from powders with different structure (Table 2). Their form is displayed in Fig. 2.

Thus, the presence of aggregates in oxide powders strongly influences the microstructure of a ceramic. A high-density, quite uniform crystalline structure of the ceramic, the structure being characterized by high parameters, specifically, the mechanical parameters, is formed only in the case of a highly dispersed powder containing no aggregates larger than 1 μm.

We know that to obtain high-density ceramic oxide materials with optimal microstructure, including optically trans-

TABLE 2.

Powder	Structure of the ceramic	Apparent density, g/cm^3	Open porosity, %
Aggregated by 20 – 30%, aggregates are dense and ≤ 25 μm in size, the rest consists of 1 – 3 μm particles	Nonuniform, large rounded 20 – 30 μm crystals and 5 – 10 μm pores are present	4.25	3.5
Almost not aggregated, particle size 1 – 2 μm	Uniformly crystalline, virtually no porosity, 20 – 25 μm crystals	4.45	0

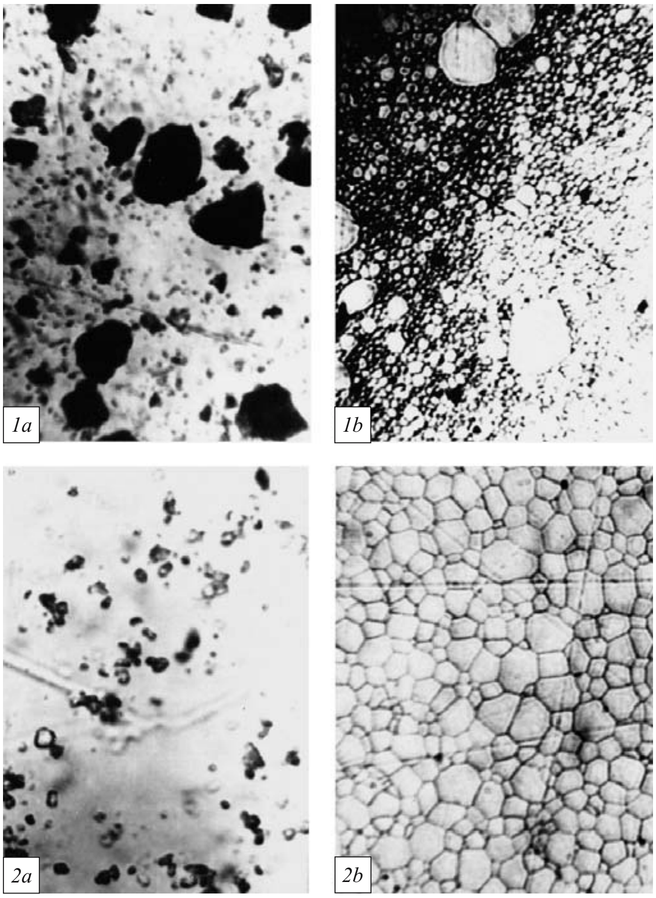

Fig. 2. Powders and microstructure of yttrium – aluminum garnet ceramic: *1a*) initial powder (× 2000); *1b*) ceramic produced from this powder (× 300); *2a*) powder comminuted after sintering (× 2500); *2b*) ceramic made from this powder (× 300).

parent or construction materials (uniform distribution of elements in a solid solution, distribution of phases relative to one another) the maximum property indicators were obtained only for powders with aggregates smaller than 1 – 2 μm. Another, no less important, condition is finding a sintering regime that gives the highest compaction. In this case, the temperature in the gas atmosphere must be taken into account.

The nature of the initial compound has a large effect on sintering. For example, yttrium oxide obtained by decomposition of yttrium carbonate at 600°C sinters at 1500°C to density about 95% of the theoretical value, while yttrium oxide obtained from yttrium oxalate sinters to this density only at 1900 – 2000°C. Magnesium oxide obtained from carbonate at 600°C is so active that during hot pressing it sinters even at temperatures 700 – 800°C practically to zero open porosity. Magnesium oxide obtained from magnesium chloride sinters very poorly.

Oxide powders obtained by thermal decomposition of salts or low-solubility compounds are characterized, ordinarily, by high concentrations of nonequilibrium defects which strongly influence sinterability; it is determined by the conditions of decomposition. Such powders are said to be active, in contrast to powders whose crystal lattice imperfection is due to equilibrium disordering of the lattice. The excess energy of one mole of matter serves as a measure of activity. It is completely obvious that the active state is unstable (metastable). When the structural elements of the lattice are quite mobile (for example, during heating) the concentration of the nonequilibrium defects decreases. The activity of oxide powders is closely related with their past chemical and thermal history.

Experience shows that the highly dispersed oxide powders obtained by chemical methods using modern technology are very active with respect to sintering. Ordinarily, the dispersity is briefly characterized as “less than one micron,” i.e., the dispersity lies in the nanometer size range. Indeed, corundum particles (i.e., α-Al_2O_3, crystal lattice parameter $c \approx 1.3$ nm) with specific surface area 100 m^2/g (BET) possess a surface-averaged diameter of 15 nm, i.e., 10 cells fit along it. Therefore, the state of the atoms making up such a particle is closer to a surface state, especially considering that when it arises under strongly nonequilibrium conditions the overlapping of the chemical bonds between neighboring atoms occurs randomly, in a disordered fashion, with a large number of different kinds of structural imperfections forming. According to the existing data, quite open particles with low values of the pycnometric density, microhardness, and refractive index are formed (see Table 1). This is due to their structure, first and foremost, the surface structure.

According to modern ideas, a perfectly smooth crystal surface can exist only at absolute zero temperature. Ya. I. Frenkel’ introduced the concept of “natural roughness” of crystals which arises on their surface as result of thermal fluctuations [8]. In addition, such roughness includes locations where dislocations, boundaries of crystals and other defects, steps — edges of atomic planes which did not completely cover a face, as well as vacancies in the surface layer and single atoms (adatoms), present on the surface, both intrinsic and extrinsic atoms, emerge at the surface. Thus, defects arise not only in the volume of a crystal but also on its surface [9]. Atoms in the layers near the surface are bound to one another more weakly and possess a higher mobility than in the interior volume. Ordinarily, it is assumed that the thickness of such a layer equals tens of interlayer distances.

Returning to the example of corundum particles, it is evident that their material is in the “surface” state. The powder particles are rounded and their crystal state is strongly distorted — they are “x-ray amorphous.” The latter signifies that they do not have a crystal lattice (since there no diffraction of x-rays by such a lattice). They are, essentially, similar to drops of a congealed liquid, the symmetry of the chemical bonds being spherical, i.e., no definite directionality exists. This is due to, first and foremost, the presence of a large number of surface defects consisting of the atoms (ions) with partially compensated chemical bonds as a result of the pre-

sence of small particles, not much larger than a unit cell on steps, protrusions, and corners.

We note that large hydrostatic compression forces arise in finely dispersed particles as result of an increase of surface tension. Thus, for particles about 1 μm in size these forces are estimated to be 0.5 MPa and they increase as particle size decreases. The surface tension forces and the high concentration of imperfections are responsible for the unstable state of a body with elevated activity. Specifically, this results in an appreciable decrease of the melting temperature of the powder as compared with a monolith [3].

Different combinations of the oxide deformation temperature and removal rates of gaseous products of decomposition make it possible to change the properties of the powders. Oxide powders which are characterized by small particles, the presence of microstresses and strains, as well as twin defects form at moderate temperatures. To ensure high sintering activity, decomposition must be conducted by rapid heating of small portions of salts or low-solubility compounds to a temperature above the decomposition onset temperature in a flow of gas which is inert with respect to the products of the reaction. The oxide powders obtained under such conditions are apparently characterized, in addition, by internal microstresses and strains as a result of the imperfection of the processes. Such a process can be implemented in practice by the method of decomposition of salts or low-solubility compounds injected in the form of concentrated solutions or suspensions, for example, hydroxides, into a high-temperature reactor. Then, decomposition occurs over a very short time and finally dispersed powders of oxides or their compounds are obtained.

Apparently, this is important for obtaining powders of individual oxides and compounds. In oxides with additives forming cell solutions, the concept of sintering activity becomes much broader. Additives form imperfections in the form of point defects, microdistortions, and deformations in the crystal lattice, which promotes high diffusion rates at all stages of sintering. The combination of activity of oxide powders, determined by the action of the additives, together with activity which is acquired as result of definite thermal conditions of synthesis makes it possible at the initial stages of sintering to have a higher rate which is primarily due to defects acquired at the stage of synthesis of powders of a solid solution. At the subsequent, especially concluding, stages of sintering the rate of the process is determined by the imperfections which the additives produce when they enter a crystal lattice. This is evidenced by, for example, the fact that yttrium oxide ceramic with added HfO_2 is obtained with the same high transparency using powders of solid solutions sintered in the temperature range 800 – 1500°C. The density and light transmission of ceramic increase somewhat with increasing temperature. Powders obtained by sintering at low temperatures start to sinter at a temperature approximately 100 – 150°C lower than powders sintered at high temperatures. However, as a result of their higher activity, individual large pores up to 0.5 mm in size are often formed; obviously, this is inadmissible for transparent ceramic.

Therefore, the optimal condition for calcinating a charge which is a solid solution is heating to a sufficiently high temperature at a high rate, which preserves the high dispersity of the powders. At low or medium temperatures the powders possess such a high activity that during sintering the particles trap pores, which then combine into large pores. Increasing the heating temperature of the charge eliminates this phenomenon and increases the uniformity of the microstructure and stability of the properties of the ceramic.

In summary, it can be supposed that defects, including those formed when additives are introduced, play a major role during sintering of oxide powders, and the technology for preparing a charge must allow high dispersity without the presence of aggregates of particles larger than 1 μm. The specific surface area of powders can be small in these cases. The action of the additives is based on the formation of structural imperfections in the form of vacancies (heterovalent additive) in the lattice or on the creation of substantial stresses in the lattice, which greatly increase the mobility of elements of the crystal lattice (isovalent additive). The basic principles for choosing the additives for the purpose of effectively influencing sintering are as follows:

the additive must form a solid solution;

the radius of a cation of the additive must differ as much as possible from the radius of a matrix atom;

additives introduced into oxide compounds must form solid solutions with each oxide comprising the compounds;

the effect of the additives intensifies when isovalent and heterovalent substitutions are used simultaneously.

Irrespective of the type of solid solution formed, the influence effect is very substantial and depends to a large degree on the gas medium during sintering. Oxides with a cubic crystal structure can sinter to a transparent state in vacuum or oxygen when such modifying additives are introduced. In anisotropic oxide materials, because of the nonuniform change in the lattice parameter during the formation of the solid solution, crystals become smaller and acquire an isometric shape.

Modifying additives which are uniformly distributed over the volume of particles of the initial powder have the most influential effect on sintering. This can be achieved either by co-precipitation or by introducing additives in the form of a soluble salt during comminution of the precipitated compound in a salt solution. The salt must be in the decomposition temperature range of the intermediate compound. Structural defects play the main role in sintering of oxide powders with additives that form solid solutions, and the technology for preparing the charge must give high powder dispersity with a uniform distribution of the components. In this case, high activity in compaction processes is observed at all stages of sintering.

REFERENCES

1. W. D. Jones, *Fundamental Principles of Powder Metallurgy*, Edward Arnold, London (1960).
2. Ya. E. Geguzin, *The Physics of Sintering* [in Russian], Nauka, Moscow (1984).
3. V. V. Skorokhod and S. M. Solonin, *Physical and Metallurgical Principles of the Sintering of Powder* [in Russian], Metallurgiya, Moscow (1984).
4. V. A. Ivensen, *Phenomenology of Sintering* [in Russian], Metallurgiya, Moscow (1985).
5. M. Yu. Bal'shin, *Powder Metal Science* [in Russian], Metallurgiya, Moscow (1948).
6. W. D. Kingery, *Introduction to Ceramics*, Wiley, New York (1960).
7. A. B. Kozlova, E. S. Lukin, D. N. Poluboyarinov, et al., "Fabrication of articles from yttrium by hot casting," *Ogneupory*, No. 9, 55 – 58 (1976).
8. Ya. I. Frenkel', *Introduction to the Theory of Metals* [in Russian], Gostekhizdat, Moscow (1958).
9. van Buren, *Defects in Crystals* [Russian translation], Inostr. Lit., Moscow (1962).